

[54] GAS ANALYZER

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[63] Continuation-in-part of Ser. No. 301,209, Oct. 26, 1972, abandoned.

[52] U.S. Cl. **250/373; 250/432; 250/573; 356/206**[51] Int. Cl. **G01n 21/26; G01n 23/12**[58] Field of Search **250/373, 573, 432, 339, 250/345; 356/206, 207, 76; 73/23**[56] **References Cited****UNITED STATES PATENTS**

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Primary Examiner—James W. Lawrence

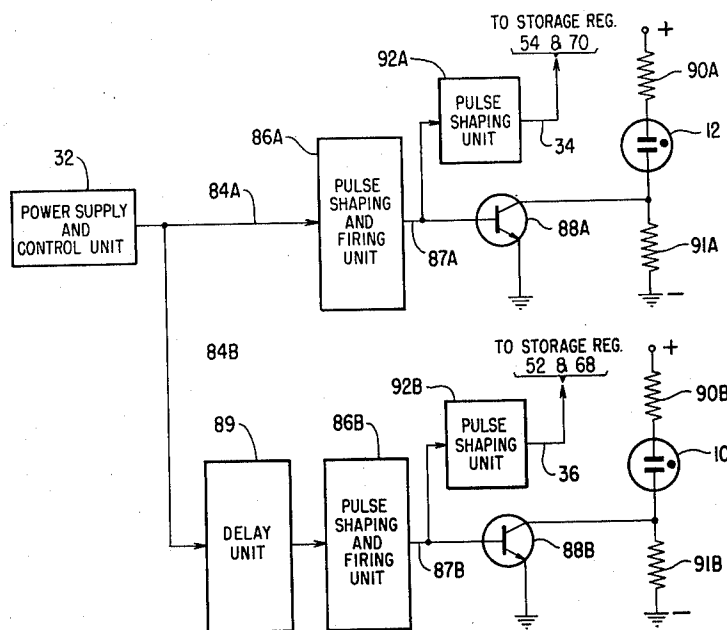
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[57]

ABSTRACT

A gas analyzer for determining the concentration of a constituent gas in a mixture of gases carrying solid particulate matter in suspension. The analyzer includes a first and a second radiation source which emit radiation of different wave lengths having different absorption coefficients for the constituent gas but virtually identical absorption coefficients for the solid particulate matter. Radiation pulses from the first and second sources are alternately passed through the gas mixture to a phototransducer generating output signals which input to a computing circuit, the output signal from which is in substantially linear proportion to the constituent gas concentration and which is unaffected by the solid particulate matter suspended in the mixture of gases. A monitoring phototransducer also receiving the radiation pulses from the radiation sources generates output signals which input to the computing circuit to compensate for deterioration and other changes in the outputs of the radiation sources.

8 Claims, 10 Drawing Figures

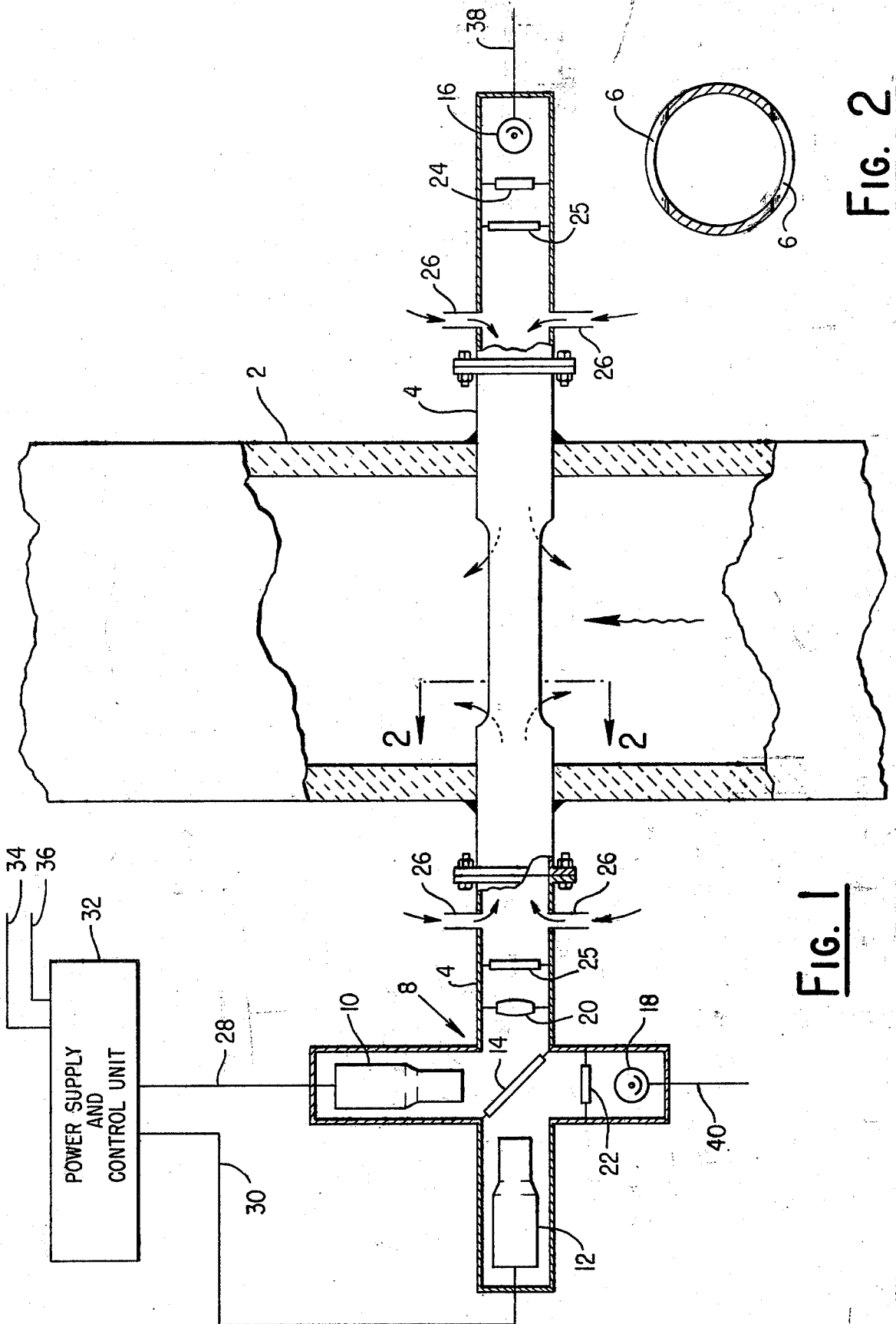


FIG. 1

FIG. 2

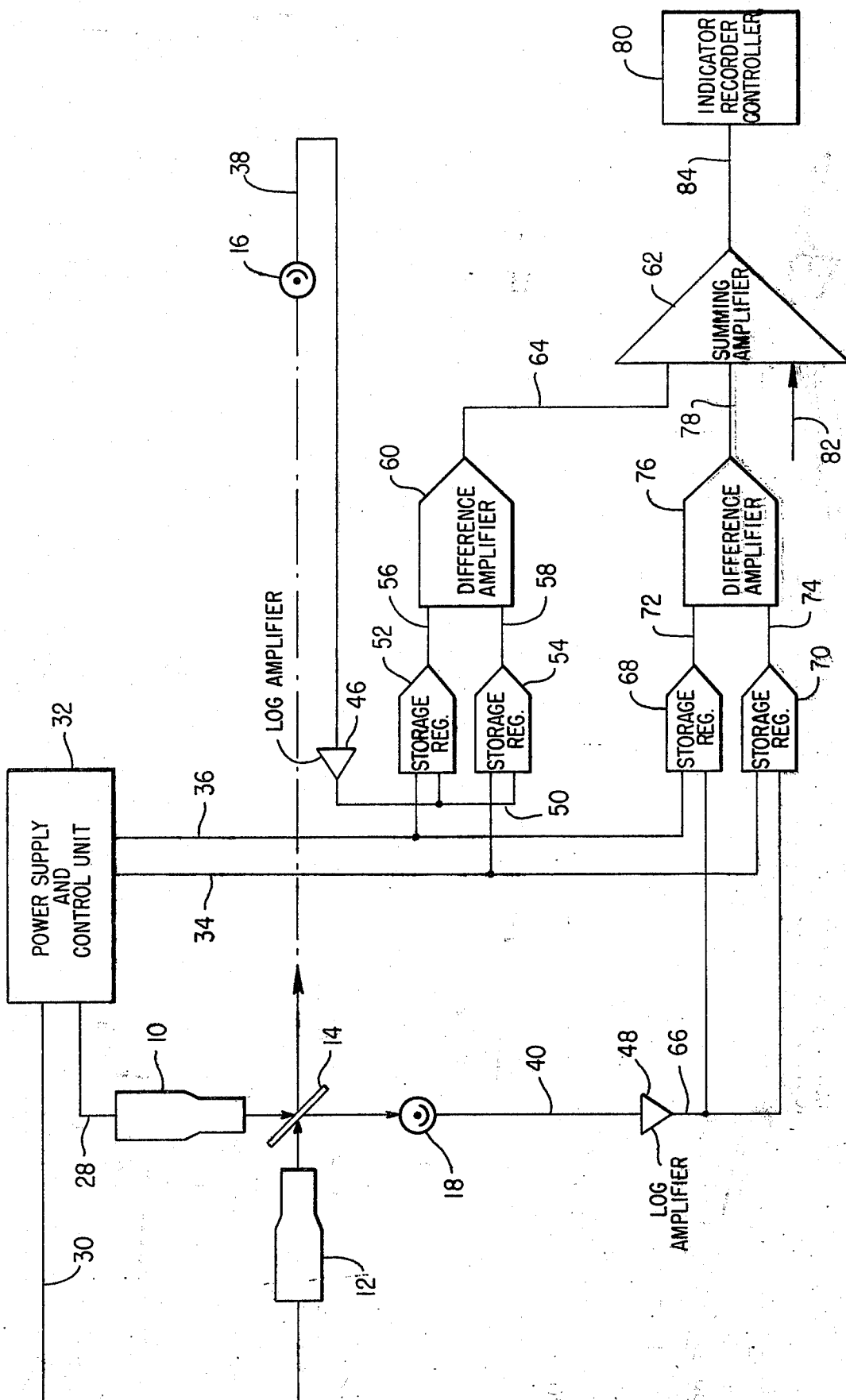


FIG. 3

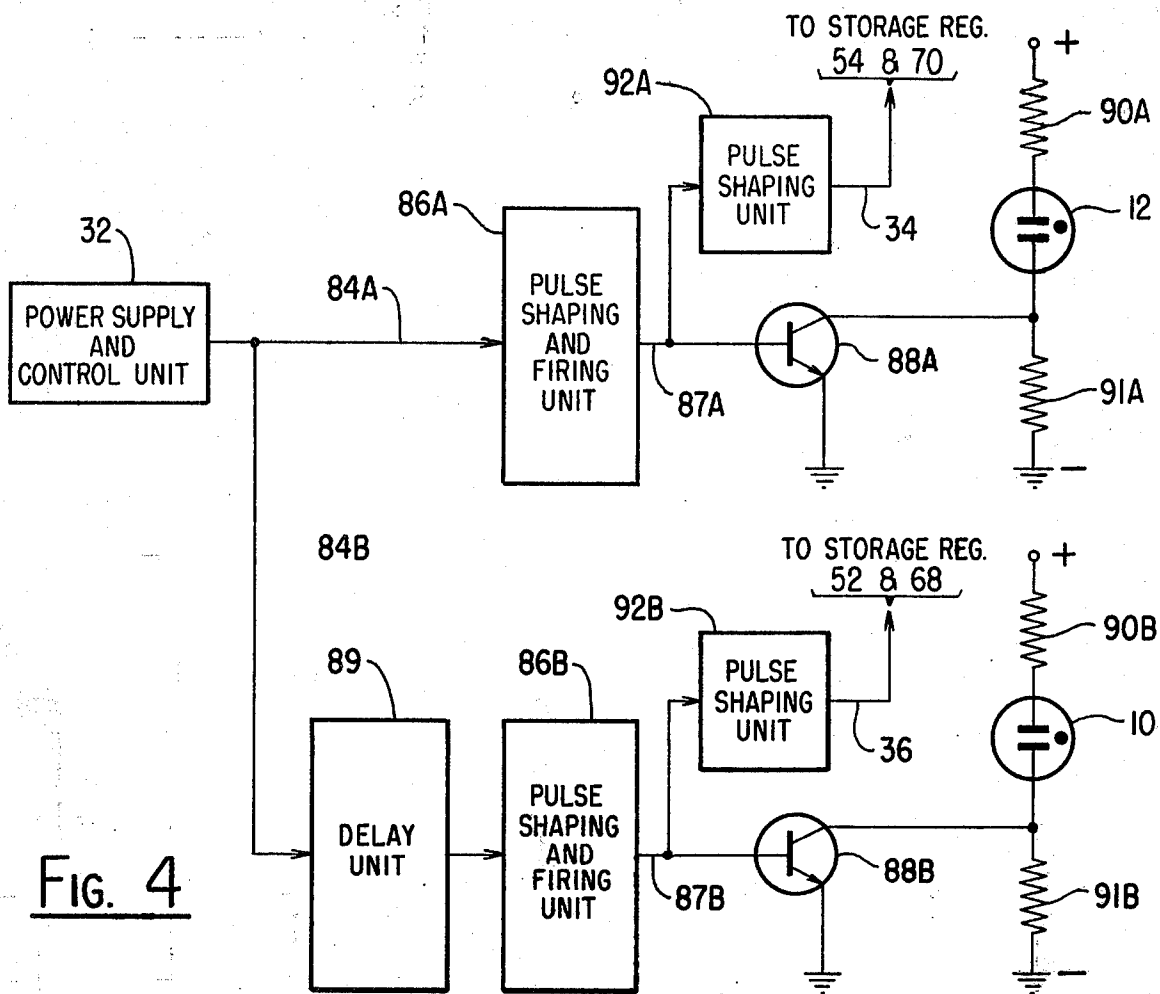


FIG. 4

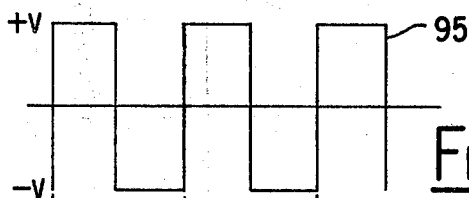


FIG. 5A

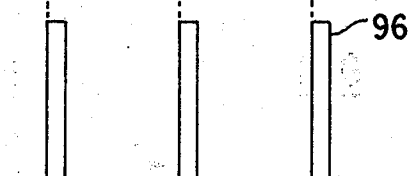


FIG. 5B

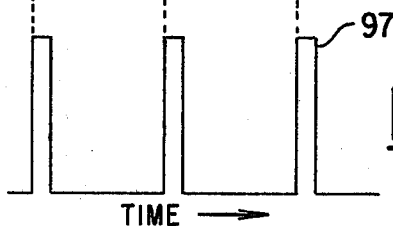


FIG. 5C

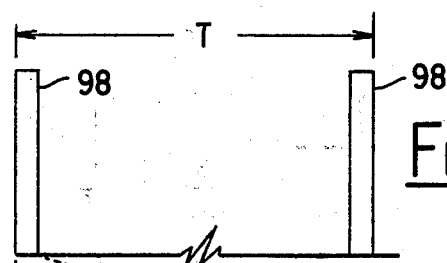


FIG. 6A

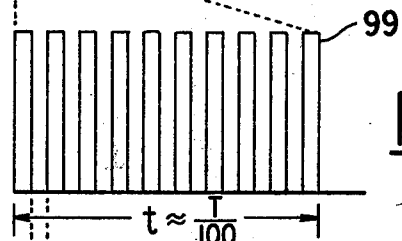


FIG. 6B

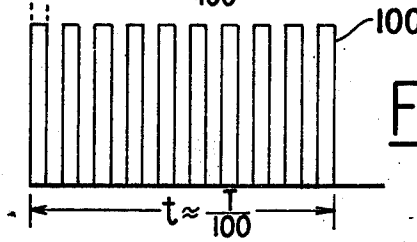


FIG. 6C

GAS ANALYZER

This is a continuation-in-part of application Ser. No. 301,209 filed Oct. 26, 1972, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to gas analyzers generally and in particular to a gas analyzer for determining the sulphur dioxide concentration in waste gases carrying solid particulate matter in suspension such as discharged to the atmosphere from industrial processes and fossil fuel fired furnaces or produced in industrial processes, such as gases produced in sulphuric acid manufacture, pulp manufacture and the like. Heretofore the concentration of SO_2 and other deleterious constituents in waste gases has received little attention, emphasis being placed on gas analyses which are indicative of the completeness or efficiency of combustion or of the process. Emphasis, however, has recently been placed on instruments which will continuously analyze for the concentration of deleterious constituent gases in waste gases. Of major importance among such deleterious constituent gases is sulphur dioxide.

Sulphur dioxide analyzers presently available are predominantly of the sampling type wherein a sample of the waste gases is intermittently or continuously withdrawn, cleaned of solid particulate matter and then analyzed by one means or another. Such analyzers are unsatisfactory for industrial purposes in that their use involves drawing the sample through a sampling line to the analyzer. Such a sampling line ordinarily must be heated to prevent water vapor or sulphuric acid condensation and it must be periodically purged to prevent plugging by solid particulate matter. Furthermore, care must be taken in selecting the materials of the sampling line lest it act as a catalyst to convert SO_2 to SO_3 and thus give an erroneous analysis. Furthermore, deposits of particulate matter in the sampling line can act as a catalyst for conversion of SO_2 to SO_3 . Such instruments draw the sample from a particular point in the flowing stream of gases and are therefore subject to error due to stratification of the SO_2 within the stream. Finally it may be said that such instruments are deficient for industrial use in that they give history rather than news. There is an unavoidable time lag in drawing the sample through a sample line, so that what is exhibited is not the SO_2 concentration presently existing but that which existed some time previously.

SUMMARY OF THE INVENTION In its broader aspects the present invention is directed to a gas analyzer for determining the concentration of a constituent gas in a mixture of gases carrying solid particulate matter in suspension. More particularly it is directed to a gas analyzer for determining the concentration of SO_2 in a mixture of gases carrying solid particulate matter in suspension.

IN THE DRAWINGS

FIG. 1 is a schematic illustration showing an in-situ application of our gas analyzer.

FIG. 2 is a cross-sectional view taken along the line 2—2 in the direction of the arrows in FIG. 1.

FIG. 3 is a schematic illustration showing in block diagram one form of computing circuit.

FIG. 4 is a schematic illustration showing in block diagram a modification of a part of the computing circuit shown in FIG. 3.

FIGS. 5A, 5B, 5C and 6A, 6B, 6C are graphs useful in explaining the operation of the modified computing circuit shown in FIG. 4.

DETAILED DESCRIPTION

For purposes of description we have chosen to illustrate and describe our invention as applied to the in-situ determination of SO_2 in waste gases flowing through a duct. However, our invention has a wide variety of other applications and may be used, for example, to determine the SO_2 concentration in gases regardless of whether or not the analysis is made in-situ. Our invention may also be used to determine the SO_2 concentration in gases produced for use in industrial processes to aid in maximizing the efficiency of production or to aid in maintaining the SO_2 concentration at, or below, or above a predetermined value.

Referring to FIG. 1 there is shown a duct 2 through which waste gases flow in the direction of the arrow. Mounted transversely in the duct is a light pipe 4 which may be of the type illustrated and described in copending application Ser. No. 348,876 filed in the U.S. Pat. Office on April 9, 1973. As shown in FIG. 1, taken in conjunction with FIG. 2, the light pipe is provided with slots 6 of predetermined length and width through which the waste gases pass.

Mounted on one end of the light pipe 4 is a housing indicated at 8 in which is mounted a hollow-cathode lamp 10 which may be from the group comprising iridium and magnesium, and of that group preferably magnesium. Also mounted in the housing 8 is a hollow-cathode lamp 12 which may be from the group comprising gallium, tin or lead, and of that group preferably gallium.

A beam-splitter 14 is disposed within the housing 8 so that radiation emitted from the lamps 10 and 12 is split, part being transmitted through the light pipe 4 to a phototransducer 16 and the remainder to a phototransducer 18. A lens, such as shown schematically at 20 may be mounted within the light pipe 4 to collimate the light from lamps 10 and 12. The lamp 10 when energized emits, predominately, radiation having a wave length of approximately 2852 Angstroms whereas the lamp 12, when energized, emits radiation of approximately 2874 Angstroms. Both lamps when energized emit some radiation of other undesirable wave lengths. To block this undesirable radiation from impinging on phototransducer 18 there is mounted within the housing 8 a narrow band pass filter 22 which peaks at $2,850\text{Å} \pm 50\text{Å}$ and has a half band width of 300Å or less. A substantially identical filter 24 is disposed in the light pipe 4 to block any stray light and the radiation of undesirable wavelengths from the lamps 10 and 12 impinging on phototransducer 16. Windows such as shown at 25 may be mounted within the light pipe 4 to isolate the waste gases and which may be maintained free of deposits of particulate matter by maintaining a flow of bleed air through ports such as shown at 26.

The lamps 10 and 12 are connected by lines 28 and 30 respectively to a power supply and control unit 32 which alternately energizes the lamps for short time increments whereby radiation pulses are transmitted sequentially from lamps 10 and 12 to phototransducers 16 and 18. As the lamps 10 and 12 are energized impulses are simultaneously sent along lines 34, 36 from the power supply 32 indicating the lamp fired.

In operation, the power supply and control unit 32 energizes, cyclically, for a short increment of time, the gallium lamp 12 causing it to emit a radiation pulse having a wavelength of approximately 2,874Å and simultaneously emits a signal along line 34 indicating that this lamp is energized. The radiation pulse from the lamp 12 impinges on the beam-splitter 14 and is both transmitted through the beam-splitter to the phototransducer 16 and reflected by the beam-splitter 14 to the phototransducer 18. During alternate increments of time, the power supply and control unit 32 energizes the magnesium lamp 10 causing it to emit a radiation pulse having a wavelength of approximately 2,852Å and simultaneously emits a signal along line 36 indicating that this lamp was energized. The radiation pulse from lamp 10 impinges on the beam-splitter 14 and is both transmitted therethrough to the phototransducer 18 and reflected thereby to the phototransducer 16. In the foregoing description reference has been made specifically to gallium and magnesium lamps. It is apparent, however, that either or both lamps may be replaced by other members of their respective groups.

Radiation traveling through the light pipe 4 will be absorbed to some extent by the particulate matter suspended in the flowing stream of waste gases as well as the SO₂ present therein, with the unabsorbed portion being received by the phototransducer 16 which produces a signal along line 38 proportional to the intensity of the unabsorbed radiation. The phototransducer 18 produces a signal proportional to the radiation to which it is exposed which is transmitted along line 40. Since there is no absorptive media between the lamps 10, 12 and phototransducer 18, changes in the output signal therefrom are indicative of deterioration or changes in the outputs of the lamps.

Referring now to FIG. 3 there is shown in block diagram one type of computing circuit whereby an output signal corresponding to SO₂ concentration in the flowing stream of waste gases can be generated. It should be understood however that the computing circuit shown is for illustrative purposes only, it being evident that any computing circuit either analog or digital may be incorporated in our invention which functions substantially in accordance with the following:

In the presence of both a gaseous absorbent and particulates, the attenuation of monochromatic light is described by:

$$-\ln \frac{I}{I_0} = k C_s L + \Phi C_p L \quad (1)$$

where:

I = intensity of light reaching phototransducer 16, watts

I_0 = intensity of light reaching phototransducer 16 in the absence of absorbing gas and particulate material, watts

k = absorption coefficient of absorbing gas, cm⁻¹

C_s = concentration of absorbing gas, mol fraction

L = light pathlength through gas, cm

Φ = extinction coefficient for particulate material, cm²/gm

C_p = concentration of particulate material, gm/cm³

Where light of two different wavelengths is concerned, for example that coming from lamps 10 and 12, respectively, this equation applies separately for both wavelengths:

$$-\ln \frac{I_a}{I_{a0}} = k_a C_s L + \Phi_a C_p L \quad (2)$$

$$-\ln \frac{I_b}{I_{b0}} = k_b C_s L + \Phi_b C_p L \quad (3)$$

where the a and b subscripts merely denote one or the other of the two wavelengths. If the wavelengths are very close together, Φ_a will be very nearly equal to Φ_b no matter what the nature of the particulates. For example, as a practical matter, if one wavelength is 1 percent than the other, then the two particulate extinction coefficients will differ by at most 4 percent, even under the most adverse conditions. Thus, as a practical matter, $\Phi_a = \Phi_b$ and equations (2) and (3) may be solved simultaneously to give:

$$C_s = \frac{\ln I_b - \ln I_{b0} - \ln I_a + \ln I_{a0}}{(k_a - k_b)L} \quad (4)$$

However, as practically, it is difficult to measure I_{a0} and I_{b0} ; I_{am} and I_{bm} that are proportional thereto may be substituted therefor:

$$I_{a0} = \alpha I_{am}; I_{b0} = \beta I_{bm}$$

where α and β are proportionality constants whose values depend upon the characteristics of beam-splitter 14. The concentration of absorbing gas is, then, given in terms of I_{am} and I_{bm} by:

$$C_s = \frac{\ln I_{am} - \ln I_a - \ln I_{bm} + \ln I_b + \ln \alpha/\beta}{(k_a - k_b)L} \quad (6)$$

The values of I_{am} and I_{bm} are measured by phototransducer 18. The term $\ln \alpha/\beta$ is merely a constant, or a zero adjustment, that is inputted into the computing circuit so as to get zero output for zero concentration of the absorbing gas.

As shown in FIG. 3 the signals generated by phototransducer 16 input to a logarithmic amplifier 46, whereas the signals generated by phototransducer 18 input to a logarithmic amplifier 48. The output signals from logarithmic amplifier 46 are applied along line 50 to storage registers 52 and 54. Registers 52 and 54 are also connected to the power supply and control unit through lines 36 and 34 respectively. The registers 52 and 54 are connected through lines 56, 58 respectively to a difference amplifier 60 connected to an algebraic summing amplifier 62 by way of line 64. The output signals from logarithmic amplifier 48 are applied along a line 66 to storage registers 68 and 70. Registers 68 and 70 are also connected to the power supply and control unit 32 through lines 36 and 34 respectively. The registers 68 and 70 connected through lines 72 and 74 respectively to a difference amplifier 76 connected to algebraic summing amplifier 62 by way of line 78. The output signal from algebraic summing amplifier 62 may be transmitted to an appropriate indicating, recording and/or controlling device such as shown at 80.

The algebraic summing amplifier 62 may be provided with a calibration input 82 which may be used, to properly adjust for the constant $\ln \alpha/\beta$ of equation (6).

In operation, the computing circuit, as shown in FIG. 3, whenever the power supply and control unit 32 ener-

gizes the lamp 10 the signal indicating such actuation is transmitted along line 36 to the registers 52, 68 causing them to receive the signals supplied from the phototransducers 16 and 18 respectively. Similarly when the power supply actuates the lamp 12 the signal indicating such actuation is transmitted along line 34 to the registers 54, 70 causing them to receive the signals then supplied from the phototransducers 16 and 18 respectively. Thus after one cycle of operation, the logarithms of values of the unabsorbed radiation from lamps 10 and 12 are stored in registers 52, 54 and the values of the logarithms of the radiation emitted from lamps 10 and 12 are stored in registers 68, 70. These values are the values of $\ln I_a$, $\ln I_b$, $\ln I_{am}$ and $\ln I_{bm}$ in equation (6) for C_s .

The registers 52, 54 provide the inputs to the difference amplifier 60 while the registers 68, 70 provide the inputs to the difference amplifier 76. The outputs of the amplifiers 60, 76 provide the inputs to the summing amplifier 62. The amplifier 62 thus provides an output along line 84 that is virtually linearly proportional to the concentration of SO_2 in the waste gases passing through the duct or stack 2 and which is substantially independent of particulate matter concentration.

From the foregoing, it is obvious that choosing the wavelengths of the hollow-cathode lamps 10 and 12 sufficiently close together will eliminate interference from particulate matter, so that a correct result is obtained regardless of the amount of particulate matter. Moreover, it will also be recognized that the same kind of compensation is afforded for interfering gases that happen to have the same absorption coefficient for both wavelengths. This is, indeed, the case with ozone, which is slightly absorbed at wavelengths in the order of 2,850Å, but with substantially the same coefficient for the radiations from both lamps. It is also obvious that gases that do not absorb appreciably in this wavelength region, for example, water vapor, carbon dioxide, oxygen, nitrogen, etc., will have no effect upon the accuracy of the analyzer. As heretofore described the power supply and control unit 32 cyclically energizes, for short increments of time, the lamp 12, and during alternate increments of time, the lamp 10. Such supervision by the power supply and control unit 32 is graphically illustrated by trace 95 in FIG. 5A. During a complete cycle of operation the unit 32 produces a positive square wave for one-half cycle having a desired time duration and a negative square wave during the following one-half cycle having the same time duration. Directly or indirectly, through conventional circuit components, the positive wave energizes the lamp 12. Simultaneously the unit generates a control signal which is transmitted along line 34 to storage registers 54 and 70. During alternate half cycles the negative wave energizes the lamp 10 and the unit simultaneously generates a control signal transmitted along line 36 to storage registers 52 and 68. Thus the lamps 10 and 12 have a 50 percent duty cycle each being energized one-half the time, regardless of the length of a complete cycle of operation.

In FIG. 4 there is shown in block diagram a modification of the circuit shown in FIG. 3 which, while retaining all of the desirable features of the latter, may be adjusted to give maximum lamp life by further reducing the lamp cycle duty, or by operating the lamps intermittently. In the latter, the lamps are energized by a periodic burst of electrical pulses, each burst of sufficient

time duration to provide sample averaging, thus compensating for momentary excursions in system parameters, such as a puff of smoke, followed by a dead time period of length consistent with the exigencies of a particular application. As an order of magnitude our invention comprehends operating the lamps at an overall 1% duty cycle or even less, as we have found that the life of the lamps is increased in inverse proportion to the reduction in duty cycle. Further we have found that in most industrial processes the composition of the gases changes relatively slowly, so that the reduction in duty cycle does not adversely affect accuracy.

Referring to FIG. 4 the square wave described in reference to FIG. 5A is transmitted along line 84A from the power supply and control unit 32 to a pulse shaping and firing unit 86A which at the start of each positive cycle, as shown by trace 96 in FIG. 5B generates a pulse which is transmitted along line 87A to the base of a transistor 88A. As evident, the unit 86A may be designed to generate a pulse of desired time duration which may be, for example, in the order of 1 percent of a complete cycle of operation.

The square wave from the power supply and control unit 32 is also transmitted along line 84B to a delay unit 89 and thence to a pulse shaping and firing unit 86B, identical with unit 86A, which following the time delay established by unit 89, as shown by trace 97 in FIG. 5C, usually corresponding to the time duration of the pulse generated in unit 86A, generates a similar pulse which is transmitted along line 87B to the base of a transistor 88B.

Except for the duration of the pulses generated in units 86A and 86B, the lamps 10 and 12 are preferably maintained energized below the threshold potential necessary to fire, by a divider network, which in the case of the lamp 12 comprises a resistor 90A connected to a positive voltage source and a resistor 91A connected to ground. A similar divider network comprising resistors 90B and 91B is provided for the lamp 10.

Transistors 88A and 88B are normally non-conducting, however, upon receiving a pulse from unit 86A or 86B respectively are rendered conducting, shorting out the resistor 91A or 91B as the case may be, thereby firing the lamp 12 or 10 to provide the intermittent and sequential operation heretofore described.

In the modification shown in FIG. 4 the control signals indicating the firing of the lamp 10 or the lamp 12 are not transmitted directly from the power supply and control unit 32, but are derived from the pulses from the unit 86A or the unit 86B. In the case of lamp 10, the pulses transmitted along line 87B are transmitted to a pulse shaping unit 92B which generates a control signal, transmitted along the line 36, to the storage registers 52 and 68. Similarly, in the case of lamp 12 the shaped pulses transmitted along line 87A are transmitted to a pulse shaping unit 92A which generates a control signal transmitted along line 34 to the storage registers 54 and 70.

The pulse shaping units 92A and 92B may, depending upon the firing characteristics of lamps 12 and 10 and circuit factors, be arranged to generate control signals having a time duration the same as, or shorter than, the time duration of the pulses generated in units 86A and 86B. We have found, however, that the control signals should preferably have a time duration which is a fraction of the time duration of the pulses. As an order of magnitude, we have found it desirable

that if the pulses generated in units 86A and 86B have a time duration of 0.003 seconds, the control signals should have a time duration of approximately 0.0003 seconds at a selected point in the time span of the pulses, thus introducing into the storage registers 52, 54, 68 and 70 output signals from phototransducers 16 and 18 having maximum integrity and eliminating spurious signal components due to the firing characteristics of lamps 10 and 12 and other factors which may be conveniently referred to as system noise.

As illustrated graphically in FIG. 6A, the power supply and control unit 32 may be arranged to generate momentary pulses 98 of any desired time period T. Each pulse so generated, transmitted along lines 84A and 84B, triggers the pulse shaping and firing units 86A and 86B to generate a burst of pulses 99 as shown in FIG. 6B, and a burst of pulses 100 as shown in FIG. 6C respectively. Each burst has a total time duration t . During a burst of pulses each lamp may be considered as having a 50 percent duty cycle, however, as the total time duration t and the number of pulses in a burst may be adjusted to the minimum required to produce an average sample during each sampling period and which is followed by a dead time period which may be, as an order of magnitude one hundred times or more in time duration than the sampling period, the overall duty cycle of lamps 10 and 12 is thus minimized, maximizing lamp life.

While as an aid to understanding our invention we have at times in the foregoing description used specific figures, it should be recognized that these are by way of example only and not by way of limitation.

We claim:

1. A gas analyzer for determining the concentration of a constituent gas in a mixture of gases containing interfering material comprising, a first and a second radiation source which emit radiation of different wave lengths having different absorption coefficients for the constituent gas and virtually identical absorption coefficients for said interfering material, means generating electric control pulses having a predetermined time period, a first means responsive to said control pulses generating a first pulse burst having a time duration substantially less than said time period, means responsive to the pulses in said first burst energizing one of said radiation sources to produce radiation pulses, a second means responsive to said control pulses for sequentially generating a second pulse burst having a time duration substantially the same as said first burst, means responsive to the pulses in said second burst energizing the other of said radiation sources to produce radiation pulses, means passing said radiation pulses through said mixture of gases to a first phototransducer producing

signals proportional to the radiation received from said first and second sources, and a computing circuit responsive to said signals generating an output signal corresponding to the concentration of the constituent gas.

2. A gas analyzer according to claim 1 further including, a second phototransducer receiving said radiation pulses and producing signals corresponding to the magnitude thereof, said computing circuit responsive to said last named signals and modifying said output signal in accordance therewith.

3. A gas analyzer as set forth in claim 2 further including a beam-splitter located proximate to said radiation sources whereby radiation pulses therefrom are split, part being transmitted to said first phototransducer and part being simultaneously transmitted to said second phototransducer.

4. A gas analyzer as set forth in claim 2 further including a first narrow band pass filter disposed between said radiation sources and said first phototransducer to block radiation of undesirable wave lengths from impinging on said first phototransducer and a second narrow band pass filter disposed between said radiation sources and said second phototransducer to block radiation of undesirable wave lengths from impinging on said second phototransducer.

5. A gas analyzer as set forth in claim 1 wherein said constituent gas is sulphur dioxide, and said first radiation source is a hollow-cathode lamp whose cathode is formed from the group consisting of iridium and magnesium and said second radiation source is a hollow-cathode lamp whose cathode is formed from the group consisting of gallium, tin and lead.

6. A gas analyzer as set forth in claim 1 further including a first means responsive to the pulses in said first burst generating a signal controlling the response of said computing circuit to the signals proportional to the radiation received from said first radiation source and a second means responsive to the pulses in said second burst controlling the response of said computing circuit to the signals proportional to the radiation received from said second radiation source.

7. A gas analyzer as set forth in claim 1 wherein said first and second means generate output signals having a predetermined time duration less than the time duration of the pulses in said first and second pulse bursts respectively.

8. A gas analyzer as set forth in claim 1 further including means continuously energizing said first and second radiation source below their firing potential and wherein said means responsive to said control pulses increases the potential across said sources above the firing potential.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3895233 Dated July 15, 1975

Inventor(s) Richard H. Boll and John E. Tozier

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 13, before "than" insert -longer-.

Signed and Sealed this

thirtieth Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks